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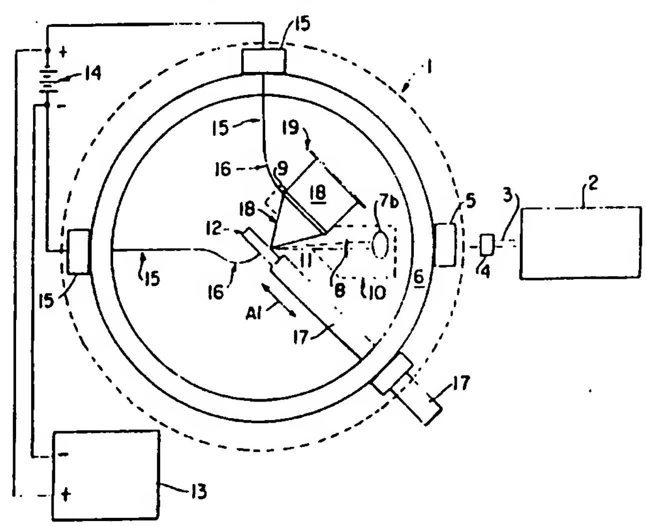


(57) Abstract

Apparatus and method for producing amorphous or microcrystalline diamond-like smooth hard coatings on ceramics, glass and plastic for protection from chemical attack and abrasion are disclosed. In vacuum chamber (1) pulsed laser (2) directs a beam (3) through optical device (4), window (5) and lens (8) with mirrors (7a, b) of scanning device (10) positioning the focused beam (11) onto carbon target (12) to produce plume (18) of vaporized material. Coatings are produced by augmenting the plume with a capacitor circuit (13, 14, 15, 16). Energy stored in a capacitor is coupled via ring electrode (9) and the target to the plume in synchronization with the pulsed laser deposition process. Augmentation of the plume increases the energy and ionization of the deposition species and aids in expanding the area of the plume to match that of the substrate (19) on which the film is to be deposited. The target position is adjusted via linear actuator (17), which with the scanning device prevents damage to the target.

* (Referred to in PCT Gazette No. 45/1996, Section II)

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# APPARATUS FOR DEPOSITING A LAYER OF MATERIAL ON A SUBSTRATE

## BACKGROUND OF THE INVENTION

The United States Government may have rights to this invention by virtue of funding under Contract No. NAS5-38069 from the National Aeronautics and Space Administration (NASA).

This invention relates to an apparatus for depositing a layer of material on a substrate, in particular, a layer such as hard diamond-like material comprising carbon and/or carbon bonded to any one or more species of boron, nitrogen or hydrogen.

Mechanical wear is a problem for almost all articles in daily use. Many products are coated with materials such as silica, alumina, boron nitride, and diamond to enhance the products' resistance to wear. In some applications, such as bar code scanners and watches, expensive sapphire plates are used instead of less expensive glass or plastic protective plates because sapphire resists scratches and is a better protective material than glass and plastic. The cost of such articles, however, increases dramatically because of the need to use the expensive wear resistant sapphire plates. For example, the price of a quartz crystal watch is approximately \$30 without a sapphire plate. The cost of a quartz watch having a sapphire coating, however, is on the order of \$300-\$1000.

There are many instances where a thin layer of a hard material is applied to and used to protect a softer material. Several techniques have been used to coat a given article with a layer of a suitable material. These techniques, including sputtering, ion beam deposition, e-beam evaporation and chemical vapor deposition, however, suffer from deficiencies when employed to deposit materials such as diamond, carbon nitride and other carbon composites. These deficiencies include high substrate temperature, low deposition rate, small

area of deposition, high cost, and poor quality (i.e., non-uniformity) of the coating.

Diamond and "diamond-like" materials (materials nearly as hard as diamond) are of particular interest for use as protective coatings because these materials have a hardness of 10 or nearly 10 compared with sapphire's hardness of 9. Diamond, while harder than sapphire, is far more expensive, and thus its use has been limited. "Diamond-like materials," as referred to in the present specification, describes materials nearly as hard as diamond comprising carbon and/or nitrogen, hydrogen, and boron. Carbon films containing hydrogen are referred to as diamond-like carbon (DLC). Only a relatively few materials have even been postulated to have hardness greater than that of diamond. $C_3N_4$ and C-B-N are among those predicted to have hardness greater than that of diamond.

Deposition of materials using lasers has been reported as early as 1968. Both a continuous wave laser and a pulsed laser have been used for thin film deposition. Subsequently, pulsed laser deposition (PLD) was used for a variety of materials like high temperature superconductors, ferroelectrics, dielectrics, metals, etc. Sato et al. of Japan, as evidenced by a paper entitled "Diamond-Like Carbon Films Prepared By Pulse Laser Evaporations," Appl. Phys. A 45, 355-360 (1988), and several others were among the first to employ this technique for the deposition of DLC films. Pulsed laser deposition has been successfully used for the deposition of diamond and diamond-like materials. However, a serious drawback of previous PLD systems has been the relatively small area of film that could be deposited by the process.

U.S. Patent No. 4,987,007 to Wagal et al., herein incorporated by reference, discloses one method of depositing DLC films using PLD. An accelerating grid spaced from a graphite target is charged to a negative potential and is used to separate carbon ions from a plume. Thus, the grid is charged to an opposite potential than the carbon ions so as to attract the ions. While the teachings of the Wagal et al. patent may provide satisfactory results in some applications,there is a need to deposit a higher quality film

than can be achieved using the Wagal et al. method. The Wagal et al. patent suggests that a higher growth rate and a quality film may be achieved by using a higher energy laser than is disclosed in the Wagal et al. patent. These higher energy lasers are costly, however.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide a superior process for the deposition of diamond and diamond-like materials including conventional diamond-like carbon, carbon nitride and C-B-N on ceramics, glass and plastic for use in a variety of applications.

It is another object of the present invention to deposit a wear-resistant coating on a large area of a substrate.

It is another object of the present invention to achieve a high deposition rate for wear-resistant coatings.

It is a further object of the present invention to deposit a DLC coating on a substrate at room temperature.

It is a further object of the present invention to reduce the need for higher power lasers and hence to reduce the associated costs in creating larger wear-resistant coatings.

In accordance with the present invention, a method and apparatus is provided for depositing high quality coatings of conventional and new materials on a substrate by a pulsed laser deposition process that includes the capacitive coupling of energy. The apparatus in accordance with the present innovation includes a pulsed evaporation means such as a pulsed electron/ion beam or a pulsed laser beam directed to impinge on a solid carbon target. When properly focused, these pulsed sources provide very high power at the focal point, evaporating the carbon or carbon composite and forming a plume. A capacitor stationed outside the vacuum chamber is discharged through a graphite ring placed between the target and the substrate. The energy stored in the capacitor is released in synchronization with the pulsed evaporation source and is applied to the plume. The energy coupled to the material plume is given by

$$E = \frac{1}{2} CV^2$$

where, C is the capacitance value of the external capacitor and V is the voltage to which it is charged. The present technique allows the variation of the energy that can be applied to the material plume by varying C. Also, by choosing a proper value for the capacitor, C, the time constant RC, which determines the time taken by the capacitor to discharge, can be controlled. Thus, by properly varying the quantity of energy and rate at which the energy is applied to the plume material, the plume may be improved to produce novel diamond-like hard layers of carbon nitride and C-B-N, and other metastable materials and enhance the quality of the layers.

## BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other features of the present invention will be more readily apparent from the following detailed description of preferred embodiments taken in conjunction with the attached drawings wherein:

Fig. 1 is a diagrammatic view of the augmented pulsed laser disposition apparatus of the present invention;

Fig. 2 is detailed illustration of the scanning device used in the present invention;

Fig. 3 illustrates the placement of the ring electrode and its relation to the target and lens of the present invention;

Fig. 4 is a graph comparing the absorption spectra of a sapphire sample with a diamond-like coating produced with the apparatus of the present invention, and a sapphire sample without the coating;

Fig. 5 is a graph comparing the absorption spectra of a thicker sapphire sample with a diamond-like coating produced with the apparatus of the present invention, and a sapphire sample without the coating; and

Fig. 6A-6B are graphs of the transmission of sapphire with and without the diamond-like coating.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Fig. 1 illustrates the preferred embodiment of the augmented pulsed laser deposition apparatus of the present invention. Referring to the figure, a vacuum chamber 1 is provided, preferably sustaining a pressure of $10^{-6}$Torr. A pulsed laser 2, preferably a pulsed Q-switched Nd:YAG laser Surelite II-10 model from Continuum, is positioned outside the vacuum chamber 1, and emits a pulsed beam 3. Alternatively, a source producing a pulsed electron/ion beam may be used. The pulsed beam 3 enters an optical device 4, such as a cross post adaptor from Newport, model CA-1, which prevents the formation of an elliptical focused spot at the carbon target 12. The beam then enters the vacuum chamber through a quartz window 5 mounted to a feedthrough collar 6.

Once the laser beam 3 has entered the vacuum chamber 1, it is directed by a mirror 7a (shown in Fig. 2), preferably a CVI Y1-1025-45, to a scanning device 10. The scanning device 10, contains a lens 8, such as a CVI PLCX-25-4/773-UV-AR/AR1064, to focus the laser beam 3 and a ring electrode 9. The focused laser beam 11 emerges from the scanning device and strikes a high purity carbon target 12 which may be obtained from Goodfellow. The lens 8 is positioned in the laser beam to assure that a minimum focused spot of the laser beam strikes the face of the carbon target 12.

Striking the carbon target with the laser beam 11 causes carbon vaporization and forms a plume of material 18. The plume of vaporized material 18 created by the laser pulse emerges from the carbon target 12 at normal incidence to the face of the target 12. Material including carbon atoms and ions pass from the face of the carbon target 12, through the ring electrode 9 and collect on the substrate 19 with the ring electrode 9 applying energy to the plume 18.

External to the vacuum chamber 1 is a high voltage power supply 13 connected in parallel to a high voltage capacitor 14 and charging the capacitor 14 to a voltage in the range of 0.5-3.0KV. The capacitor 14, preferably 0.1-0.5$\mu$f, is connected in series between the carbon target 12 and ring electrode 9 by high voltage feedthroughs 15 and flexible

conductors 16. The polarity of the ring electrode 9 is maintained at positive high voltage while the carbon target 12 is negative in polarity.

The capacitor 14 discharges the instant the plume 18 is formed during a laser pulse since the plume 18, in effect, completes the circuit and provides a path for the capacitor 14 to discharge. One skilled in the art will appreciate that no special trigger circuitry is needed due to the manner in which the circuit elements are arranged.

The resulting discharge of energy into the plume 18 increases ionization and dramatically increases the diameter of the plume and area of the film that can be deposited. Specifically the additional energy from the capacitor 14 excites carbon atoms to much higher energy states than if the capacitor 14 was not used. This results in uniform, large area films with improved adherence to the substrate 19. Thus the capacitive augmentation reduces the need for higher power lasers and hence the associated cost.

The power density present in the focused spot of the laser beam can severely erode the carbon target 12 in a short period of time. Not only is the carbon target 12 damaged but the quality of the DLC film can be compromised as well. A method and apparatus that moves the carbon target 12 and simultaneously scans the laser beam 11 thus changing the location on the carbon target 12 where the laser beam 11 is focused has been devised as a solution to this problem. The carbon target 12 is moved horizontally using a motorized linear actuator 17, such as a model VF-165-2 from Huntington Mechanical Lab, mounted to the feedthrough collar 6 and extending into the chamber 1. The carbon target 12, mounted at the end of the linear actuator 17, moves in the direction indicated by the arrow A1.

Damage to the carbon target 12 is further reduced by a scanning device 10 that moves the focused laser beam vertically. Details of the scanning device 10 are shown in Fig. 2 & 3. Referring to Fig. 2, the laser beam 3 enters the chamber via a quartz window 5 and is turned 90 degrees by a stationary mirror 7a, such as a CVI Y1-1025-45, fixed to the

chamber baseplate 20. A second mirror 7b, such as a CVI Y1-1025-45, redirects the laser beam so that it passes through the lens 8. The mirror 7b, ring electrode 9 and lens 8 are mounted on a bracket 21 that is attached to the shaft of a second motorized linear actuator 22 fixed to the chamber baseplate 20. As the motorized linear actuator 22 is operated, the distance between mirrors 7a and 7b changes depending on the direction of motion of the actuator 22. This results in a corresponding change in the position of the focused laser beam 11 emerging from the scanning device 7.

The placement of ring electrode 9 on the bracket 21 further aids the deposition of DLC films since the position of the plume 18 will move in concert with the movement of the focused laser beam 11. Fig. 3 shows a top view of scanning device 10 in more detail.

The combined motion of both linear actuators results in the focused laser beam 11 scanning the carbon target 12 in a raster pattern. In a preferred embodiment, the focused laser beam 11 is constantly moved via scanning device 10 while the carbon target 12 is periodically advanced as the laser beam 11 reaches its lowest or highest point of travel. The continuously moving plume 18 created by the capacitively augmented PLD yields hard, uniform DLC films on substrates of large areas.

Figs. 4 and 5 graphically compare the absorption spectrum of a sapphire sample coated using the apparatus of the present invention with that of an uncoated sapphire sample. In Fig. 4, the spectra of an uncoated (curve 1) and coated (curve 2) 1/8 inch sapphire sample is illustrated. The uncoated sapphire sample spectrum (curve 1) exhibits an absorption peak at approximately 200nm, however the remaining portions of the spectrum covering the UV-visible region show the uncoated sapphire is near transparent, exhibiting only approximately 5% absorption. The spectrum of the coated sapphire sample (curve 2) exhibits substantially similar absorption characteristics. The approximately 5% difference between the two spectra (curve 1 and curve 2) at 250nm decreases as the wavelength is increased, with the difference

at 900nm being negligible.

Fig. 5 illustrates the spectrum of an uncoated 1/4 inch sapphire sample (curve 1) as compared to the spectrum of an coated sapphire sample of the same thickness (curve 2). Both the uncoated and coated samples (curve 1 and curve 2) show heavy absorption near the 200nm end of the spectrum. At a wavelength of approximately 250nm, the coated sample (curve 2) absorbs approximately 5% more than does the uncoated sample (curve 1). However, as the wavelength is increased, the difference between the two absorption spectra decreases until it is negligible at 900nm.

Finally, Fig. 6A and 6B show the transmission, as measured in a spectrometer, of sapphire one-eight inch thick samples. Fig. 6A graphically illustrates the transmission of an uncoated sample, and Fig. 6B illustrates the transmission of a sample coated with a 50Å thick diamond-like coating produced with the method and apparatus of the present invention. As is clearly shown, the coating has no measurable effect of the transmission of the sapphire in the entire spectrum. Both spectra show a drop in transmission with the longer wavelengths, but this is intrinsic to sapphire.

It is clear from the graphs of Figs. 4, 5, 6A, and 6B, a diamond-like coating produced with the method and apparatus of the present invention is transparent to wavelengths in the ranges of 250-900nm and 2500-10,000nm.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

WHAT IS CLAIMED

1. Apparatus for producing a layer of material on a substrate comprising:

a vacuum chamber;

means for directing a laser beam along a first path of travel;

means for holding a target material at a target location within the vacuum chamber generally along the first path of travel;

means disposed along the first path of travel for focusing the laser beam at the target location, the laser beam being sufficiently energetic so that, when so focussed at the target location, a plume comprising at least ions of the target material is ejected from the target material along a second path of travel;

electrode means disposed within the vacuum chamber and chargeable at an electrical potential and positioned adjacent to the plume, the electrical potential being the same polarity as the ions; and

means for supporting the substrate in the vacuum chamber and disposed along the second path of travel for collecting the ions on the substrate to produce the layer of material on the substrate.

2. Apparatus according to claim 1, wherein the vacuum chamber includes a window and the laser beam is created outside the chamber, with the first path of travel traversing the window.

3. Apparatus according to claim 1, wherein the target material comprises carbon.

4. Apparatus according to claim 3 wherein the layer of material is diamond-like carbon.

5. Apparatus according to claim 3 wherein the layer of material is carbon nitride.

6. Apparatus according to claim 1 further comprising:

means electrically connected to the target material and the electrode means so that the two are held at opposite polarities prior to the formation of the plume.

7. Apparatus according to claim 1 further comprising:

means for selectively moving the target material so that the laser beam strikes the target material sequentially at a plurality of locations on the target material.

8. Apparatus according to claim 1 further comprising:

means for sequentially aiming the laser beam at a plurality of locations on the target.

9. Apparatus according to claim 8 further comprising:

means for moving the electrode means in concert with the movement of the laser beam from one location to another on the target material.

10. Apparatus according to claim 1 further comprising:

an electrical energy source; and

an electrical energy storage device electrically connected to the electrical energy source, and electrically connected to the electrode means so that the storage device is charged by the electrical energy source and discharges upon formation of the plume thereby charging the electrode means.

11. Apparatus according to claim 10 further comprising:

means of selectively moving the target material so that the laser beam strikes the target material sequentially at a plurality of locations on the target material.

12. Apparatus according to claim 10 further comprising:

means for sequentially aiming the laser beam at a plurality of locations on the target.

13. Apparatus according to claim 10 further comprising:

means for moving the electrode means in concert with the movement of the laser beam from one location to another on the target material.

14. Apparatus according to claim 10, wherein the target material comprises carbon.

15. Apparatus according to claim 10 wherein the layer of material is diamond-like carbon.

16. Apparatus according to claim 10 wherein the layer of material is carbon nitride.

17. Apparatus for producing a layer of material on a substrate comprising:

a vacuum chamber;

means for directing a laser beam along a first path of travel;

means for holding a target material at a target location within the vacuum chamber generally along the first path of travel;

means disposed along the first path of travel for focusing the laser beam at the target location, the laser beam being sufficiently energetic so that, when so focussed at the target location, a plume comprising at least one of atoms and ions of the target material is ejected from the target material along a second path of travel;

electrode means disposed within the chamber and chargeable at an electrical potential and positioned adjacent to the plume;

an electrical energy source;

an electrical energy storage device electrically connected to the electrical energy source, and electrically connected to the electrode means so that the storage device is charged by the electrical energy source and discharges upon formation of the plume thereby charging the electrode means;

and means for supporting the substrate disposed along the second path of travel for collecting at least one of atoms and ions from the plume on the substrate to produce a layer of material on the substrate.

18. Apparatus according to claim 17, wherein the vacuum chamber includes a window and the laser beam is created outside the chamber, with the first path of travel traversing the window.

19. Apparatus according to claim 17 wherein the target material comprises carbon.

20. Apparatus according to claim 19 wherein the layer of material is diamond-like carbon.

21. Apparatus according to claim 19 wherein the layer of material is carbon nitride.

22. Apparatus according to claim 17 wherein the electrical energy storage device is additionally connected to the target material so that electrode means and the target material are held at opposite polarities prior to the formation of the plume.

23. Apparatus according to claim 17 further comprising:

means for selectively moving the target material so that the laser beam strikes the target material sequentially at a plurality of locations on the target material.

24. Apparatus according to claim 17 further comprising:

means for sequentially aiming the laser beam at a plurality of locations on the target.

25. Apparatus according to claim 24 further comprising:

means for moving the electrode means in concert with the movement of the laser beam from one location to another on the target material.

26. An apparatus for producing a film on a substrate comprising:

a chamber;

means for creating a vacuum within the chamber;

means for directing a laser beam along a first path of travel;

means for holding a target material at a target location within the chamber generally along the first path of travel;

means disposed along the first path of travel for focusing the laser beam at the target location, the laser beam being sufficiently energetic so that, when so focussed at the target location, a plume of material is ejected from the target material along a second path of travel;

electrode means disposed within the chamber and chargeable at an electrical potential and positioned adjacent to the plume;

an electrical energy source;

an electrical energy storage device electrically connected to the electrical energy source, and electrically connected to the electrode means so that the storage device is charged by the electrical energy source and discharges upon formation of the plume thereby charging the electrode means; and

means for supporting the substrate disposed along the second path of travel for collecting the material from the plume on the substrate to produce a layer of material on the substrate.

27. Apparatus according to claim 26, wherein the vacuum chamber includes a window and the laser beam is created outside the chamber, with the first path of travel traversing the window.

28. Apparatus according to claim 26, wherein the target material comprises carbon.

29. Apparatus according to claim 28 wherein the layer of material is diamond-like carbon.

30. Apparatus according to claim 28 wherein the layer of material is carbon nitride.

31. Apparatus according to claim 26 wherein the electrical storage device is additionally connected to the target material so that the electrode means and the target material are held at opposite polarities prior to the formation of the plume.

32. Apparatus according to claim 26 further comprising:

means for selectively moving the target material so that the laser beam strikes the target material sequentially at a plurality of locations on the target material.

33. Apparatus according to claim 26 further comprising:

means for sequentially aiming the laser beam at a plurality of locations on the target.

34. Apparatus according to claim 33 further comprising:

means for moving the electrode means in concert with the movement of the laser beam from one location to another on the target material.

35. A method for producing a layer of material on

a substrate comprising the steps of:

creating a substantially vacuum atmosphere in a chamber;

directing a laser beam along a first path of travel;

holding a target material at a target location in the chamber generally along the first path of travel;

focusing the laser beam at the target location, the laser beam being sufficiently energetic so that, when so focussed at the target location, a plume of material is ejected from the target material along a second path of travel to create a plume comprising at least ions along a second path of travel;

charging the plume with a voltage at the same polarity as ions within the plume; and

collecting material from the plume on a substrate.

36. The method of claim 35 wherein the substantially vacuum atmosphere is at a pressure of $10^{-6}$Torr.

37. The method of claim 35 wherein the charging step comprises:

charging an electrical storage device;

discharging the electrical storage device upon the creation of the plume thereby charging the plume.

38. The method of claim 35 further comprising the step of:

moving the target material so that the laser beam strikes the target material sequentially at a plurality of locations on the target material.

39. The method of claim 35 further comprising the step of:

sequentially aiming the laser beam at a plurality of locations on the target.

40. The method of claim 39 further comprising the step of:

moving an electrode means in concert with the movement of the laser beam from one location to another on the target material.

41. A method for producing a layer of material on a substrate comprising the steps of:

creating a substantially vacuum atmosphere in a chamber;

charging an electrical storage device;

directing a laser beam along a first path of travel;

holding a target material at a target location in the chamber generally along the first path of travel;

focusing the laser beam at the target location, the laser beam being sufficiently energetic so that, when so focussed at the target location, a plume of material is ejected from the target material along a second path of travel to create a plume comprising at least ions along a second path of travel;

discharging the electrical storage device thereby charging the plume with a voltage; and

collecting material from the plume on a substrate.

42. The method of claim 41 wherein the substantially vacuum atmosphere is at a pressure of $10^{-6}$Torr.

43. The method of claim 41 further comprising the step of:

moving the target material so that the laser beam strikes the target material sequentially at a plurality of locations on the target material.

44. The method of claim 41 further comprising the step of:

sequentially aiming the laser beam at a plurality of locations on the target.

45. The method of claim 44 further comprising the step of:

moving an electrode means in concert with the movement of the laser beam from one location to another on the target material.

FIG. 1

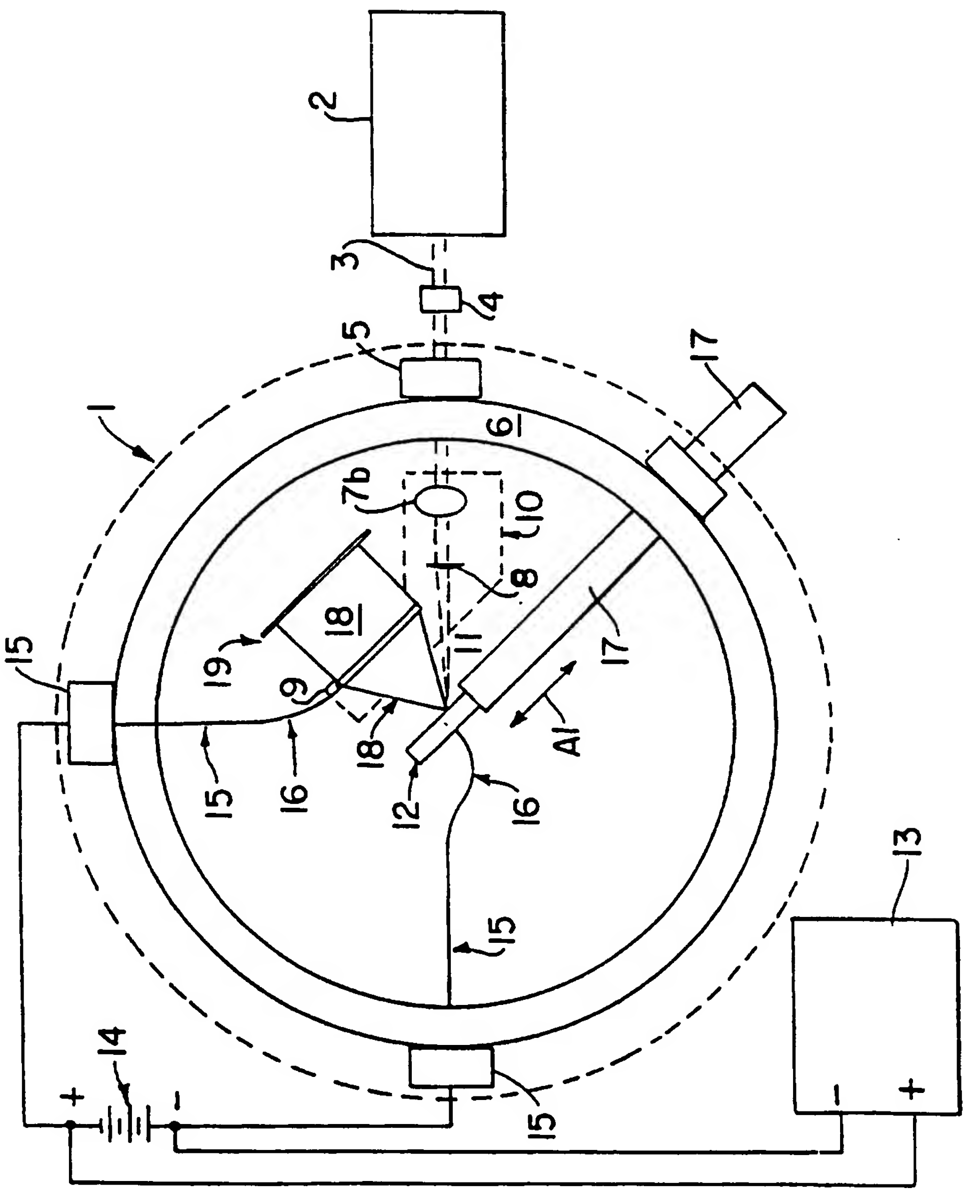


FIG. 2

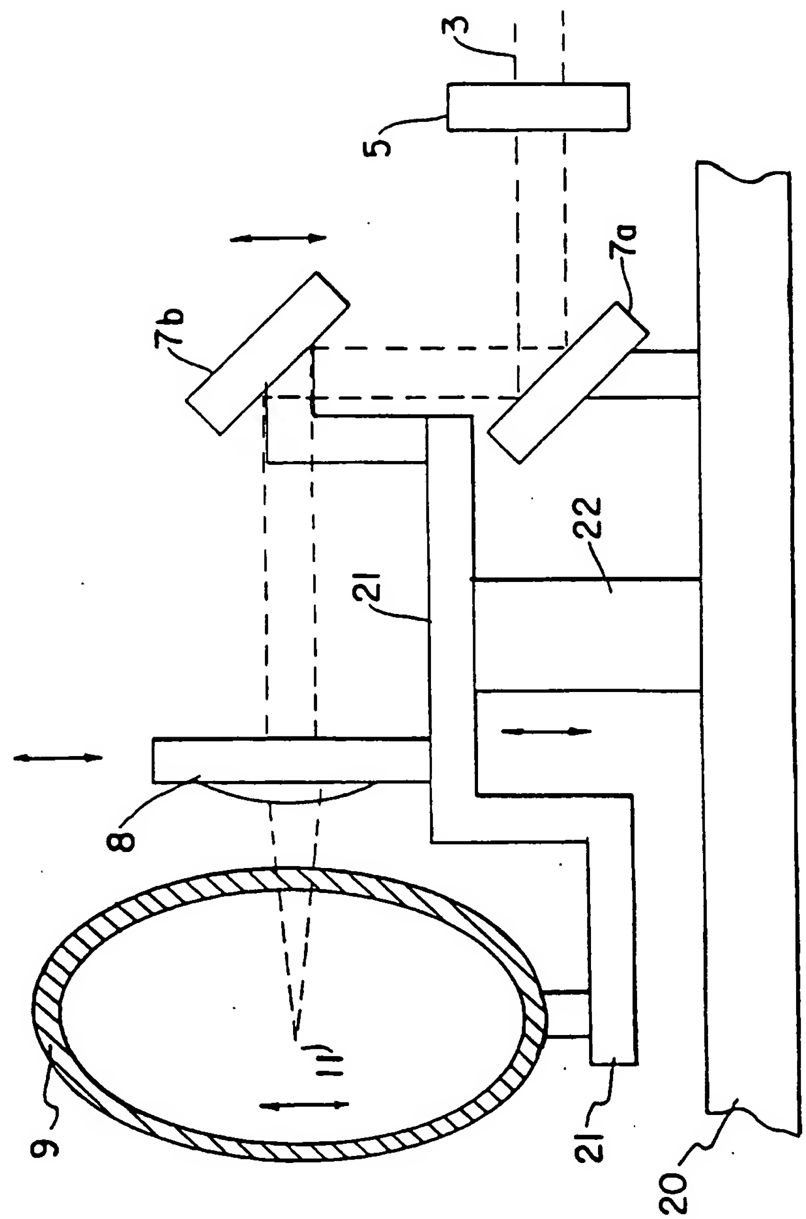


FIG. 3

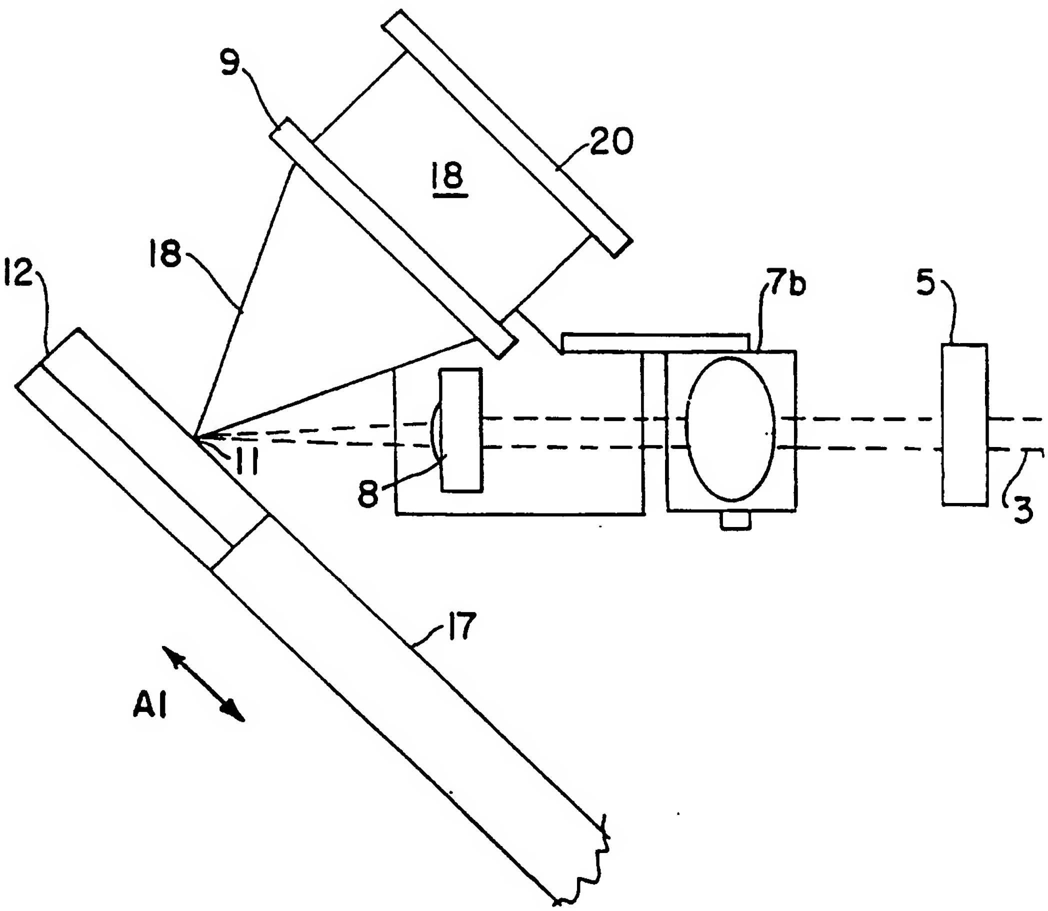


FIG. 4

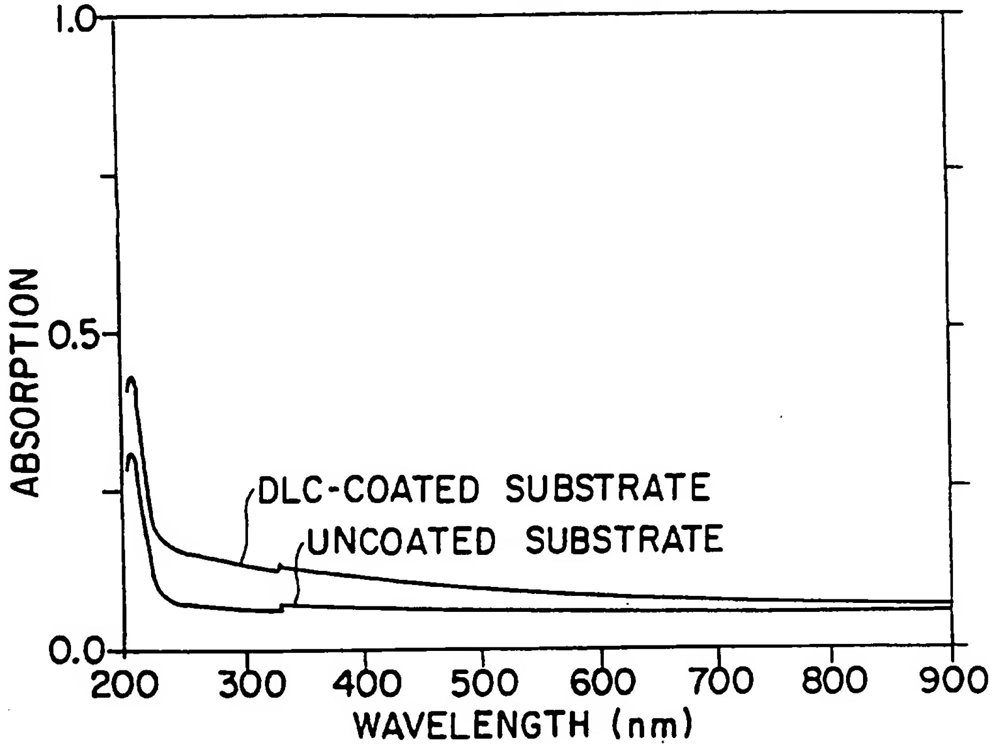
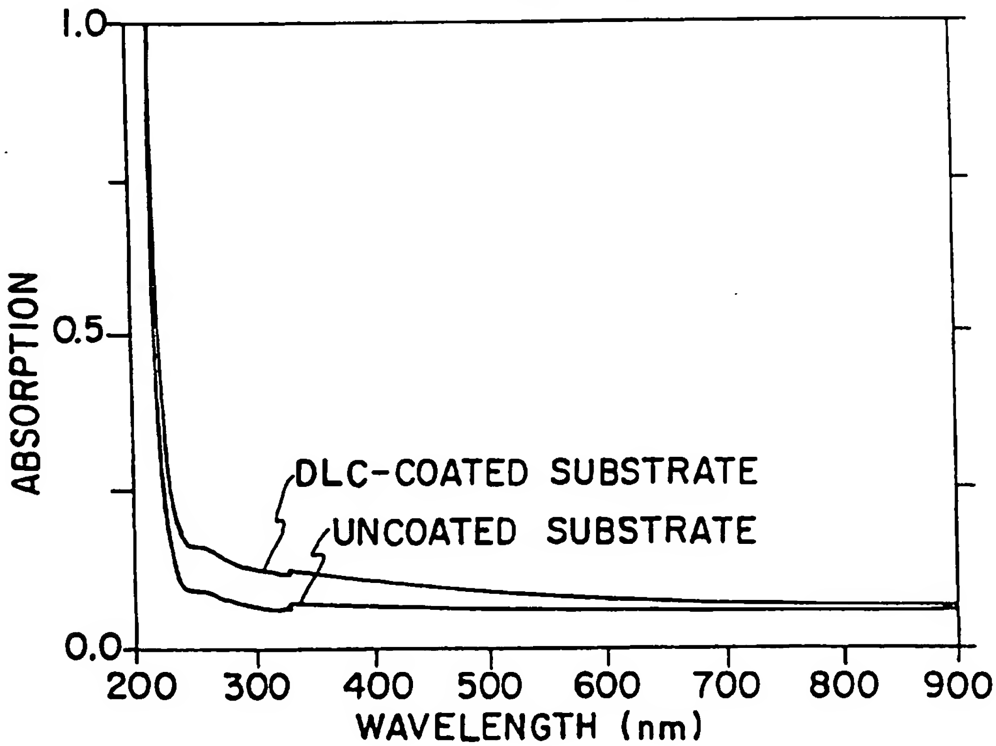

1.0
0.5
0.0
ABSORPTION
DLC-COATED SUBSTRATE
UNCOATED SUBSTRATE
200
300
400
500
600
700
800
900
WAVELENGTH (nm)

FIG. 5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0.5
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ABSORPTION
DLC-COATED SUBSTRATE
UNCOATED SUBSTRATE
200
300
400
500
600
700
800
900
WAVELENGTH (nm)

5/5

FIG. 6A

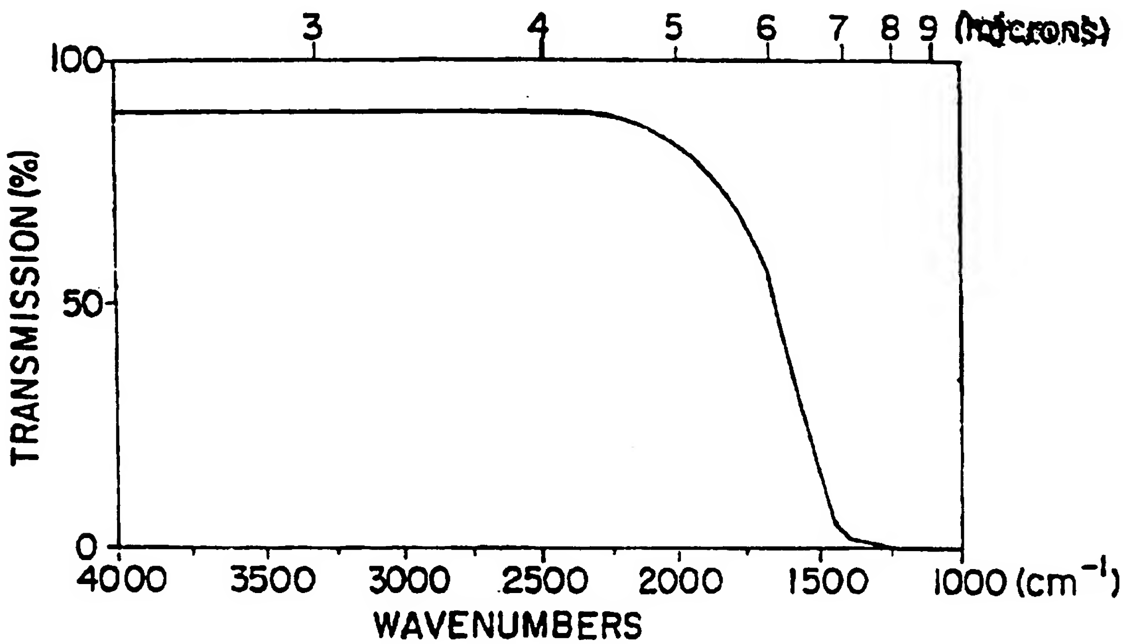
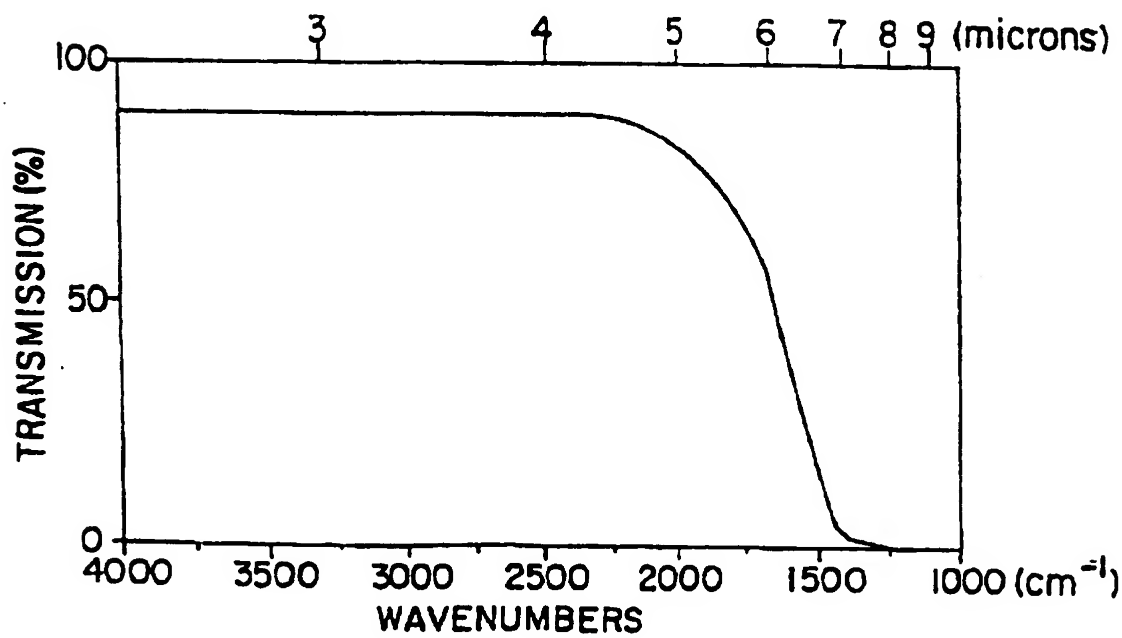



FIG. 6B



# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/13585

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :HO5B 7/20; C23C 14/06, 14/28 14/32
US CL :427/561, 562, 572, 596; 118/723 VE, 723MP, 727,50.1
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/561, 562, 572, 677, 596; 118/723 VE, 723MP, 727,50.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>---<br>Y | US, A, 5,098,737 (COLLINS ET AL) 24 MARCH 1992, SEE FIGS. 1 AND 2; COL. 4, LINES 54-68; COL. 7, LINES 11-COL 8, LINE 10 AND LINES 22-36; AND COL 6, LINES 50-57. | 1-8, 35-36 38-39<br>---------<br>9-34, 37, 40-45 |
| X<br>---<br>Y | US, A, 4,370,176 (BRUEL) 25 JANUARY 1983, SEE FIGURE; COL 3, LINE 58- COL 4, LINE 64. | 1-5, 7-8, 10-12, 14-21, 23-24, 26-30, 32-33, 35-45<br>----------<br>4-6, 9, 13, 22, 25, 31 AND 34 |
| Y | US, A, 4,664,940 (BENSOUSSAN ET AL) 12 MAY 1987, SEE ABSTRACT AND FIGURE. | 9,13,25, 34 |

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 31 JANUARY 1996 | 12 MAR 1996 |

| Name and mailing address of the ISA/US | Authorized officer |
|---|---|
| Commissioner of Patents and Trademarks<br>Box PCT<br>Washington, D.C. 20231 | MARIANNE L. PADGETT |
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## INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/13585

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US, A, 4,701,592 (CHEUNG) 20 OCTOBER 1987, SEE ABSTRACT AND FIGURES. | 1-2, 7-8, 11-13, 23-25, 32-35, 38-40, 43-45 |
| A | US, A, 5,084,300 (ZANDER ET AL) 28 JANUARY 1992, SEE ABSTRACT AND FIGURES. | 1-2, 7-8, 11-13, 23-25, 32-35, 38-40, 43-45 |
| A | US, A, 4,762,975 (MAHONEY ET AL) 09 AUGUST 1988, SEE ABSTRACT AND FIGURES. | 1-45 |
| A | US, A, 5,330,968 (NAGAISHI ET AL) 19 JULY 1994, SEE ABSTRACT AND FIGURES. | 1-45 |
| A | US, A, 5,300,485 (YOSHIDA ET AL) 05 APRIL 1994, SEE ABSTRACT AND FIGURES. | 1-45 |
| A | US, A, 5,203,929 (TAKAYANAGI ET AL) 20 APRIL 1993, SEE ABSTRACT AND FIGURES. | 1-45 |
| A | US, A, 4,987,007 (WAGAL ET AL) 22 JANUARY 1991, SEE ABSTRACT AND FIGURES. | 1-45 |
| A | US, H, 872 (HENDRICKS) 01 JANUARY 1991, SEE ABSTRACT AND FIGURES. | 1-45 |